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ORIGINAL ARTICLE

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Achillea aleppica and *Achillea arabica* (Asteraceae) Phytochemical FT-IR Analysis

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Achillea genus is a flowering, aromatic and perennial herbs, and widespread all over the world. Plants phytochemical analysis has a capital role in pharmaceutical and medicine preliminary studies. Two medicinal *Achillea* species of *A. aleppica* DC and *A. arabica* Kotschy grown wild in the Middle-Southern regions of Syria were investigated for their phytochemical analysis using fourier-transform infrared (FT-IR) spectroscopy. FT-IR spectra highlighted 11 and 12 functional groups characteristics for *A. aleppica* and *A. arabica* species, respectively; of which 9 were common between the two studied species [Aromatics (1), Ethers (3), Carboxylic acids (2), Olefinic (alkene) (1), Alkanes (1) and Aliphatic primary amine (1) groups]. These constituents have been previously investigated for different biological activities. The current study could consider as the first report regarding FT-IR *Achillea* analysis.

Key words: Achillea aleppica, Achillea Arabica, Phytochemical analysis, FT-IR

Achillea genus belongs to Asteraceae family the largest angiosperms' family that involves approximately 1500 genera and 23000 species, distributed in three subfamilies and seventeen tribes. This genus included 115 species of perennial herbs; all of them are native to temperate regions of the northern hemisphere (Heywood, 1998; Moradkhani *et al.*, 2012).

Plants phytochemical analysis using different analytical methods has a capital role in pharmaceutical and medicine studies for plants essential oils in particularly and crude extracts analysis. Among them, ultraviolet (UV), infrared spectroscopy (IR) and mass spectrometry (MS) (Stojanović *et al.*, 2005; Moradkhani *et al.*, 2014); nuclear magnetic resonance (NMR) (Moradkhani *et al.*, 2012; 2014); fourier transform infrared spectroscopy (FTIR) (Dev *et al.*, 2017); gas chromatography-mass spectrometry (GC-MS) (Dev *et al.*, 2017; Albayrak and Silahtarlıoğlu, 2020; Saleh, 2019); high-performance liquid chromatography (HPLC) (Albayrak and Silahtarlıoğlu, 2020); high-performance liquid chromatography with diode array detector (HPLC-DAD)(Şabanoğlu *et al.*, 2019) and recently, fourier transform infrared photoacoustic spectroscopy (FTIR-PAS) and diffuse reflectance infrared spectroscopy (FTIR-DRIFT) (Brangule *et al.*, 2020) and others.

Achillea species exhibited wide range in medicine and pharmaceutical applications; *e.g*. as antimicrobial (Stojanović *et al.*, 2005; Toncer *et al.* 2010; Tabanca *et al.*, 2011; Albayrak and Silahtarlıoğlu, 2020); antioxidant (Toncer *et al.*, 2010; Manayi *et al.*, 2012; Polatoglu *et al.*, 2013; Albayrak and Silahtarlıoğlu, 2020); insecticidal (Toncer *et al.*, 2010; Tabanca *et al.*, 2011; Polatoglu *et al.*, 2013); herbicidal (Toncer *et al.*, 2010; Polatoglu *et al.*, 2013); cytotoxic (Albayrak and Silahtarlıoğlu 2020); antinociceptive and anti-inflammatory (Toncer *et al.*, 2010) properties. Moreover, they used in traditional remedies against rheumatic pain and digestive complaints, fever, common cold, pneumonia and hemorrhage (Manayi *et al.*, 2012). Başer (2016) reviewed 31 *Achillea* species for their essential oil yield and composition.

The genus *Achillea* is represented in Syrian Flora with about 9 species (Mouterde, 1983), of which *A. aleppica* DC and *A. arabica* Kotschy (Synonyms. *Achillea biebersteinii* Afanasiev) were wild grown in Syria.

No information available regarding the two previous *Achillea* species in respect to their phytochemical analysis in Syria. Thereby, the current study aimed to study their phytochemical analysis using FT-IR spectra for the first time.

MATERIALS AND METHODS

Plant materials and samples preparation

Aerial parts of *A. aleppica* (A.A) and *A. arabica* (A.R) (10 plants for each species) were harvested and bulked as representative for each *Achillea* sp. Sampling has been performed during blooming stage from two wild *Achillea* species grown in their natural habitat from Middle-Southern regions in Syria. *Achillea aleppica* DC was collected from rural Damascus regions; whereas, *Achillea arabica* Kotschy was collected from rural Homs regions (Table 1).

Samples were shade dried for two weeks, and were milled to fine powder by special electric mill and stored separately in glass bowls until FT-IR analysis.

FT-IR assay

The fine powder was used as template for FT-IR analysis in the wavenumber range of 4000-500 cm^{-1}. IR measurement has been performed using NXR FTIR (Thermo, USA) instrument for FT-IR analysis.

RESULTS AND DISCUSSION

Phytochemical analysis of wild *A. aleppica* and *A. arabica* medicinal species grown in the Middle-Southern regions of Syria, has been assessed using FT-IR spectroscopy. FT-IR spectra of the *A. aleppica* and *A. arabica* aerial parts was presented in Figure 1. FT-IR analysis showed 11 and 12 functional groups characteristics for *A. aleppica* and *A. arabica* species, respectively; of which 9 were commonly sharing between the two studied species (Table 2). These common peaks were: 800 cm^{-1} (assigned to =C-H oop bend-Aromatics group); 1080, 1100 and 1700 cm^{-1} (assigned to C–O secondary alcohol stretch C–O stretch-Ethers group), 1200 and 1300 cm^{-1} (assigned to C–O stretch-Carboxylic acids group), 1630 cm^{-1}

[(assigned to Alkenyl C=C stretch-Olefinic (alkene) group], 2924 cm^{-1} (assigned to C–H stretch –Alkanes group) and 3400 cm^{-1} (assigned to NH stretch-Aliphatic primary amine group).

Saeidnia *et al.* (2011) reviewed the *Achillea* phytochemistry and reported that terpenoids (monoterpenes, sesquiterpenes, diterpenes, triterpenes), phenolic acids, flavonoids, coumarins and sterols have been frequently reported as secondary metabolites in *Achillea* species.

Başer (2016) reported the presence of camphor, 1,8-cineole, p-cymene, α-pinene, α-terpineol, α-bisabolol oxide, T-cadinol, caryophyllene oxide and spathulenol as a main components in *A. aleppica* essential oils.

Different researches focused on *A. arabica* Kotschy (Synonyms. *Achillea biebersteinii* Afanasiev) essential oils (EOs) composition; *e.g*. Tabanca *et al.* (2011) reported the presence of camphor, 1,8-cineole, borneol, p-cymene and piperitone in its EOs. Whereas, these components were camphor, 1,8-cineole, piperitone, p-cymene and ascaridol (Toncer *et al.*, 2010). Moreover, Polatoglu *et al.* (2013) reported that camphor, 1,8-cineole, α-thujone, p-cymene, ß-thujone, borneol and piperitone were presented in its EOs. Whereas, Şabanoğlu *et al.* (2019) reported the analyzed of some phenolic components, *e.g.* gallic acid, chlorogenic acid, caffeic acid, ferulic acid, *p*-coumaric acid, rutin, quercetin, luteolin, apigenin and kaempferol in three methanolic *Achillea* species (*A. biebersteinii, A. setacea* and *A. wilhelmsii* leaf, flower and root) extracts using HPLC-DAD analysis.

Other researches focused on phytochemical analysis of other *Achillea* species; *e.g.* Stojanović *et al.* (2005) reported the presence of alkanes, fatty acids, monoterpenes, guaiane sesquiterpenes (rupicolin A and B, 1-deoxy-1alpha-peroxy-rupicolin A and B), and flavonoids (apigenin and centaureidin) in *A. clavennae* (hexane:ether:methanol=1:1:1) extract using different spectral analyses (1D and 2D NMR, UV, IR and MS). Whereas, Manayi *et al.* (2012) reported the presence of sterols, tannins and terpenoids in methanolic *A. tenuifolia* root extract; whereas, sterols and terpenoids were presented in its Ethyl acetate one in preliminary test. Whereas, Moradkhani *et al.* (2012) reported for the first time the presence of β-sitosterol (compound1), 5-hydroxy, 4',6,7– trimethoxy flavone (salvigenin compound 2), and methyl-gallate (compound 3) in dichloromethane fraction *A. tenuifolia* using NMR and Mass spectral analyses. Moreover, Moradkhani *et al.* (2014) reported for the first time the presence of two known flavones 3', 5- dihydroxy- 4', 6, 7- trimethoxy flavone (eupatorine, compound 3), 5- hydroxy- 3',4', 6, 7- tetramethoxyflavone (compound 4), besides stearic acid (compound 1), lupeol (compound 2), daucosterol (β- sitosterol 3-O- β- D- glucopyranoside, compound 5), 2, 4- dihydroxy methyl benzoate (compound 6) in the methanolic *A. tenuifolia* extract using UV, IR, Mass and 1H- NMR (1D and 2D) and 13C-NMR.

More attention has been given to *A. millefolium* phytochemical analysis; *e.g.* Dias *et al.* (2013) reported higher content of fat and saturated fatty acids, proteins, ash, energy value, sugars and flavonoids in commercial methanolic *A. millefolium* (yarrow) compared to wild one. Whereas, the wild type showed higher carbohydrates, organic acids, unsaturated fatty acids, tocopherols and phenolic acids content compared to cultivated one, using HPLC analysis. Whereas, Georgieva *et al.* (2015) investigated phytochemicaly (phenolic acids, flavonoid aglycones and flavonoid glycosides) the aqueous *A. millefolium* inflorescences and upper leaves extracts using HPLC analysis.

Table 1: Collection sites of *A. aleppica* and *A.arabica* species.

Species	Collection site	Code	Altitude (m)	Annual rainfall (mm)
A. aleppica	Damascus	A.A	950	260
A. arabica	Homs	A.R	265	400

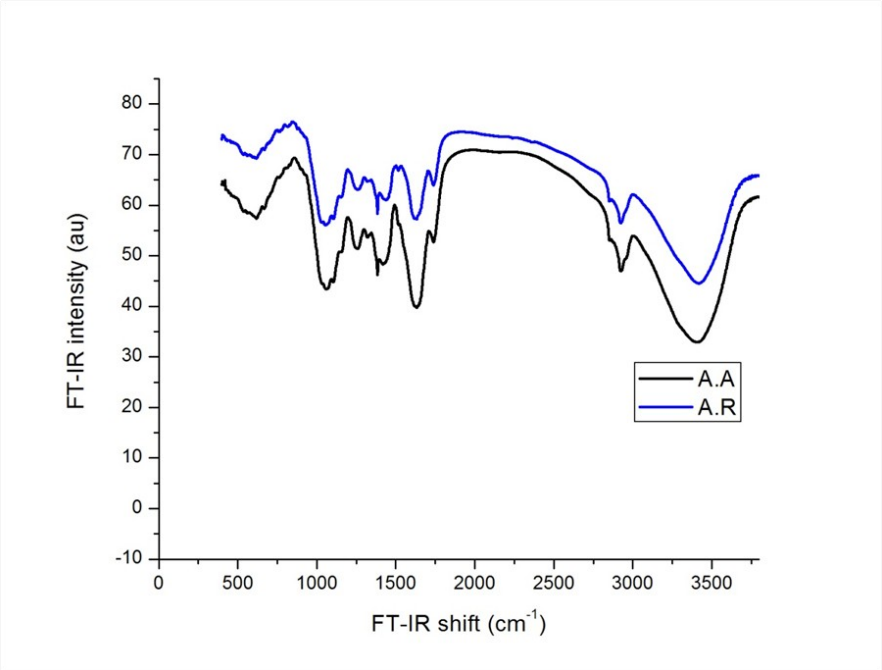

Figure 1. : FT-IR spectra of ***A. aleppica*** **(A.A) and** ***A.arabica*** **(A.R) species.**

Table 2: Observed functional groups identified in *A. aleppica* and *A.arabica* species using FT-IR analysis.

Species	Peak N°	IR frequency (cm^{-1})	Observed IR (cm^{-1})	Bond	Functional groups
A. aleppica	1	700-600	617	Aliphatic bromo compounds, C–Br stretch	Aliphatic organohalogen
	2	900-690	800	=C-H oop bend	Aromatics
	3	2000-1000	1080	C–O secondary alcohol stretch C–O stretch	Ethers
	4	2000-1000	1100	C–O secondary alcohol stretch C–O stretch	Ethers
	5	1300-1200	1200	C–O stretch	Carboxylic acids
	6	1300-1200	1300	C–O stretch	Carboxylic acids
	7	1600-1400	1417	C=C stretch aromatic	Aromatics
	8	1680-1620	1630	Alkenyl C=C stretch	Olefinic (alkene)
	9	2000-1000	1700	C–O secondary alcohol stretch C–O stretch	Ethers
	10	2970-2850	2924	C–H stretch	Alkanes
	11	3400-3380	3400	NH strech	Aliphatic primary amine
A. arabica	1	900-690	810	=C-H oop bend	Aromatics
	2	2000-1000	1080	C–O secondary alcohol stretch C–O stretch	Ethers
	3	2000-1000	1100	C–O secondary alcohol stretch C–O stretch	Ethers
	4	1300-1200	1200	C–O stretch	Carboxylic acids
	5	1300-1200	1300	C–O stretch	Carboxylic acids
	6	1600-1400	1400	C=C stretch aromatic	Aromatics
	7	1600-1400	1515	C=C stretch aromatic	Aromatics
	8	1680-1620	1630	Alkenyl C=C stretch	Olefinic (alkene)
	9	2000-1000	1700	C–O secondary alcohol stretch C–O stretch	Ethers
	10	2970-2850	2924	C–H stretch	Alkanes
	11	3400-3380	3400	NH strech	Aliphatic primary amine
	12	3645-3630	3645	primary alcohol, OH stretch	Alcohol and hydroxyy compound

CONCLUSION

Phytochemical analysis of *A. aleppica* and *A. arabica* species grown wild in Syria was investigated using FTIR assay. FT-IR spectra highlighted 11 and 12 functional groups characteristics for *A. aleppica* and *A. arabica* species, respectively; of which 9 were common between the two studied species. Whereas, Aliphatic bromo compounds, C–Br stretch-Aliphatic organohalogen functional group was observed in *A. aleppica* and not in *A. arabica* species. While, primary alcohol, OH stretch-Alcohol and hydroxy compound functional group was observed in *A. arabica* and not in *A. aleppica* species. These constituents have been previously investigated for different biological activities. The current study could consider as the first report regarding FT-IR *Achillea* analysis.

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CONFLICTS OF INTEREST

The author declares no conflicts of interest.

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